

**REMARKS**

Claims 1, 3, 4, 8, 10, 12, 15-17 and 25-65 are pending in this application. Claims 1 and 46 have been amended. No new matter has been introduced.

At the outset, Applicants note that the claimed invention is directed to, among other things, a gas conduit connecting the product chamber (or "spent fuel" chamber) to the fuel chamber, the conduit being provided with a check valve to prevent pressure equalization of the fuel and spent fuel chambers via the conduit line (i.e., gas and/or liquid can flow into the fuel chamber through the check valve, but gas and/or liquid cannot exit the fuel chamber via the check valve). Any pressure in the fuel chamber can only be released by pushing fuel out through the catalyst chamber. The claimed invention does not require a pumping system, a compressor, or other auxiliary systems to supply fuel to the catalyst chamber ("fuel is delivered to a catalyst chamber by means of internally generated differential pressure without requiring an elaborate electrically powered pumping system"; see ¶ [0001] of Applicants' specification, emphasis added). The claimed invention further comprises a first chamber configured to store a reactant material, and a second chamber configured to (i) receive borate and hydrogen gas and (ii) to store the borate separate from the reactant material ("the fuel and spent fuel are separated from each other avoiding constant dilution of the fuel concentration" and the "spent fuel collected in chamber 30"; see ¶ [0022], emphasis added).

**35 U.S.C. § 103**

Claims 1, 25-29, 31, 32, 46, 47 and 49 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Kojima (U.S. Patent Appl. Pub. No. 2001/0022960) in view of Edlund et al. (U.S. Patent No. 6,375,906) or Davenport (U.S. Patent No. 4,012,016). Applicants respectfully traverse this rejection.

Amended independent claim 1 recites "an arrangement for generating hydrogen" comprising "a catalyst chamber comprising a catalyst," "a fuel chamber connected to the catalyst chamber . . . configured to store a reactant material" and "a spent fuel chamber connected to the catalyst chamber" configured "to receive borate and hydrogen gas" and "to retain the borate separate from the reactant material." Amended independent claim 1 also recites "a gas conduit in direct communication with the spent fuel chamber and with the fuel chamber . . . including a check valve" and "a hydrogen gas outlet conduit connected to the gas conduit."

Independent claim 25 recites an "[a]pparatus for use in a system for generating hydrogen" comprising "a fuel container having an internal pressure," "a reactant material capable of generating hydrogen disposed within said fuel container, said fuel container having an outlet port which can be opened and closed, said internal pressure pushing said reactant material through said outlet port when it is open," and "a product container." Independent claim 25 also recites "a gas conduit between the product container and the fuel container," and "a check valve in communication with said gas conduit, the check valve being configured to allow the hydrogen to flow in one direction."

Amended independent claim 46 recites an "arrangement for generating hydrogen gas" comprising "a catalyst chamber comprising a catalyst," "a fuel chamber connected to the catalyst chamber . . . configured to retain a reactant material under a predetermined pressure," "a spent fuel chamber connected to the catalyst chamber . . . configured to retain the borate separate from the reactant material," "a gas conduit between the spent fuel chamber and fuel container" and "a check valve in communication with said gas conduit."

Kojima refers to a hydrogen generating apparatus comprising a storage tank or "first container" 1 containing a reactant material capable of generating hydrogen connected to a catalyst chamber or "second container" 2 via pipe 3 provided with a throttle valve 6 for controlling the flow of reactant material (see [0074]) to the catalyst chamber. A pipe 7 carries product materials and unreacted reactant material from the catalyst chamber to a hydrogen separator 8. A hydrogen gas outlet connected to separator 8 removes hydrogen from the system for supply to a reaction cell [0075]. A compressor 10 "for stably supplying the complex metal hydride solution" is connected to the pipe 9 [0074].

The subject matter of claims 1, 25-29, 31, 32, 46, 47 and 49 would not have been obvious over Kojima in view of Edlund or Davenport. The October 23, 2006 Office Action fails to establish a *prima facie* case of obviousness. Courts have generally recognized that a showing of a *prima facie* case of obviousness necessitates three requirements: (i) some suggestion or motivation, either in the references themselves or in the knowledge of a person of ordinary skill in the art, to modify the reference or combine the reference teachings; (ii) a reasonable expectation of success; and (iii) the prior art references must teach or suggest all claim limitations. See e.g., In re Dembiczak, 175 F.3d 994 (Fed. Cir. 1999); In re Rouffet, 149 F.3d 1350, 1355 (Fed. Cir. 1998); Pro-Mold & Tool Co. v. Great Lakes Plastics, Inc., 75 F.3d 1568, 1573 (Fed. Cir. 1996).

In the present case, Kojima, Edlund and Davenport, considered alone or in combination, do not disclose, teach or suggest all limitations of independent claims 1, 25 and 46. Kojima does not disclose, teach or suggest "a spent fuel chamber connected to the catalyst chamber" being configured "to receive borate and hydrogen gas" and "to retain the borate separate from the reactant material," as claims 1 and 46 recite. The system of Kojima includes a separator 8 connected to the storage tank 1 via line 9 and to

the catalyst container 2 via line 3 to isolate the hydrogen that is generated by the contact of the complex metal hydride solution and catalyst, by separating the "unreacted complex metal hydride and generated hydrogen from each other," returning the metal hydride to the storage tank and supplying the hydrogen to a cell. See Kojima at ¶¶[0074] and [0075]. Thus, in Kojima, a complex metal hydride solution is recovered and returned to the storage tank 1.

The hydrolysis reaction of a complex metal hydride such as sodium borohydride (the preferred fuel for use with Kojima's system as disclosed in paragraph [0067]) results in the formation of hydrogen and a metal borate salt, as evidenced by the equation in paragraph [0008] of Kojima;  $\text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4 \text{H}_2$ . There is no suggestion or teaching by Kojima that this non-gaseous metal borate salt product is separated from the complex metal hydride remaining in solution or otherwise retained in the hydrogen separator, but only that "hydrogen obtained in this apparatus is isolated by the hydrogen separator 8" [0074] and the "unreacted complex metal hydride isolated by the hydrogen separator 8 is returned to the storage tank 1" [0076] via pipe 9. One skilled in the art would thus expect that the unreacted metal hydride material isolated by the hydrogen separator 8 is contaminated with the metal salt product material, resulting in a continuous dilution of reactant material in the storage tank 1.

Referring now to a recent paper by Kojima et al. (attached hereto) that further describes the hydrogen generation system of the cited Kojima reference, Kojima et al. teach that it is necessary to "keep the liquid state of  $\text{NaBO}_2$  which is a byproduct" (Section 2, page 1030, "Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide." *International Journal of Hydrogen Energy*, 27, (2002) 1029-1034). Consequently, this further confirms that the complex metal hydride solution returned to the storage tank of Kojima would contain the borate salt, which is

generated with the hydrogen produced upon contacting the borohydride solution with the hydrogen generation catalyst.

Accordingly, there is no disclosure or suggestion in Kojima that separator 8 of Kojima would "retain borate and hydrogen gas" wherein the borate is "separate from the reactant material," as in independent claims 1 and 46 of the present invention. The hydrogen separator of Kojima, an integral component of Kojima's hydrogen generation apparatus, is not a spent fuel chamber configured to retain the borate separate from the reactant material, as in the claimed invention.

In addition, the system of Kojima requires a compressor to bring the fuel into contact with the catalyst as no other device or method is suggested ("according to such a hydrogen generation apparatus, the complex metal hydride aqueous solution 4 is supplied from the storage tank 1 to the catalyst container 2 with its amount of supply being adjusted by the throttle 6 and compressor 10"). There is no suggestion that the system disclosed by Kojima would be operable without the compressor and throttle valve. In contrast, claim 25 recites a fuel container having an internal pressure, said internal pressure pushing the reactant material through an outlet port. Consequently, the claimed invention does not require a pumping system, compressor, or other auxiliary systems to supply fuel to the catalyst chamber ("fuel is delivered to a catalyst chamber by means of internally generated differential pressure without requiring an elaborate electrically powered pumping system" (see ¶¶ [0001] and [0021] of the Applicants' specification, emphasis added)). Kojima nowhere discloses the internal pressure limitation of claim 25.

Edlund and Davenport fail to remedy any of the deficiencies of Kojima. None of Edlund and Davenport discloses, teaches or suggests "a fuel chamber connected to the catalyst chamber" configured to store a reactant material," "a spent

fuel chamber" configured "to receive borate and hydrogen gas" and to "retain the borate separate from the reactant material," and "a gas conduit" with "a check valve," as claims 1 and 46 recite.

Kojima, Edlund and Davenport, considered alone or in combination, also do not disclose, teach or suggest all limitations of independent claim 25. None of the cited references teaches or suggests "a fuel container having an internal pressure" and "a reactant material capable of generating hydrogen disposed within said fuel container, said fuel container having an outlet port which can be opened and closed, said internal pressure pushing said reactant material through said outlet port when it is open," as independent claim 25 recites.

For at least these reasons, the Office Action fails to establish a *prima facie* case of obviousness, and withdrawal of the rejection of claims 1, 25-29, 31, 32, 46, 47 is respectfully requested.

#### Provisional Double-Patenting Rejection

Claims 25-29, 31, 32, 46, 47 and 49 stand rejected under the judicially-created doctrine of obviousness-type double patenting as being unpatentable over claims 1-13 of co-pending Application Serial No. 10/638,651, filed on August 11, 2003; and over claims 1-45 of co-pending Application Serial No. 10/115,269, filed on April 2, 2002. Applicants submit that these rejections are provisional and that Applicants will respond to these rejections upon the indication of allowable subject matter.

#### Double Patenting Rejections

##### The '847 Patent

Claims 25-29, 31, 32, 46, 47 and 49 stand rejected under the judicially-created doctrine of obviousness-type double patenting as being unpatentable over claims 1-34 of U.S. Patent No. 6,932,847 ("the '847 patent"). Applicants respectfully traverse this rejection.

Claims 1-10 of the '847 patent recite a system for hydrogen generation comprising a first container and a second container (wherein at least a portion of at least one side of the first container is shared with at least a portion of at least one side of the second container defining a shared partition a portion of which is flexible), a catalyst system, and a pumping system. Claims 11-21 of the '847 patent recite a system for hydrogen generation comprising a first container at least partially contained within a second container, a catalyst system, a pumping system, and a spent fuel line at least partially wrapped around the second container. Claims 22-24 of the '847 patent recite a system for hydrogen generation comprising a first container, a second container, a catalyst system, a pumping system, and a spent fuel line at least partially wrapped around the second container. Claims 25-34 of the '847 patent recite an apparatus for hydrogen generation comprising a first container and a second container with at least one shared portion that responds to reactant material exiting through said exit port so as to decrease the volume of said first container and increase the volume of said second container.

A rejection under the judicially created doctrine of obviousness-type double patenting is only appropriate if the subject matter claimed in the application is merely an obvious variation of the invention claimed in a referenced patent. The disclosure of a referenced patent may not be used as prior art. *See* MPEP § 804.II.B.1. The nonstatutory double patenting analysis parallels the analysis under 35 U.S.C. § 103. *Id.*

The Office Action's assertion that claims 25-29, 31, 32, 46, 47 and 49 "recite

only the limitations which are recited in claims 1-34" of the '847 patent is unavailing. (September 8, 2005, Office Action at 10). First, claims 25-29, 31, 32, 46, 47, and 49 of the present application have been amended since September 8, 2005. They recite limitations not present in the claims of the '847 patent. For example, claims 25-29, 31, 32, 46, 47 and 49 of the present application recite an apparatus or arrangement for generating hydrogen comprising "a gas conduit between the product container and the fuel container" and "a check valve in communication with said gas conduit." Claim 46 further recites "a fuel chamber connected to the catalyst chamber" and "a spent fuel chamber connected to the catalyst chamber."

Second, a mere possibility that a claimed invention could further include additional limitations is not the standard for rejection under the doctrine of obviousness-type double patenting. It is well established that the claims must be an obvious variation of the cited reference to support a rejection under this doctrine. See MPEP § 804.II.B.1. The Office Action, however, has not set forth any reasoning why one of ordinary skill in the art, having reviewed the '847 patent claims, would consider the pending claims 25-29, 31, 32, 46, 47 and 49 an obvious variation of the '847 patent claims.

Claims 1-34 of the '847 patent do not recite "a reactant material capable of generating hydrogen disposed within said fuel container, said fuel container having an outlet port which can be opened and closed, said internal pressure pushing said reactant material through said outlet port when it is open," as recited in independent claim 25. Claims 1-34 of the '847 patent also do not recite "a fuel chamber connected to the catalyst chamber . . . configured to retain a reactant material under a predetermined pressure" or "a spent fuel chamber connected to the catalyst chamber . . . configured to retain the borate separate from the reactant material," as claim 46 recites. Accordingly, claims 25-29, 31, 32, 46, 47 and 49 are not obvious variations of claims 1-34 of the '847



patent. For at least these reasons, withdrawal of this rejection is respectfully requested.

### The '657 Patent

Claims 1, 25-29, 31-32, 46-47 and 49 stand rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-18 of U.S. Patent No. 7,083,657 ("the '657 patent"). Applicants respectfully traverse this rejection.

Claims 1-18 of the '657 patent recite a hydrogen generation system comprising "a fuel supply reservoir containing an aqueous solution," a fuel pump, "a gas-liquid separator configured to separate said fluid stream into a gaseous product comprising hydrogen and water vapor, and a liquid comprising water and said metal salt," "a condenser in fluid flow communication with said gaseous product to condense water," "a condensate recovery zone configured to recover said condensed water" and "a mixing zone configured to combine said condensed water with said aqueous solution of metal hydride."

Claims 1, 25-29, 31-32, 46-47 and 49 of the present application are patentably distinct as these claims recite limitations that are not obvious from claims 1-18 of the '657 patent. Claims 1, 25-29, 31-32, 46-47 and 49 of the present application recite an apparatus or arrangement for generating hydrogen comprising "a gas conduit between the product container and the fuel container" and "a check valve in communication with said gas conduit." Claims 1 and 46 further recite "a fuel chamber connected to the catalyst chamber" and "a spent fuel chamber connected to the catalyst chamber . . . configured to receive borate and hydrogen gas . . . and to retain the borate separate from the reactant material." In contrast, the claims of the '657 patent only recite "a fuel

supply reservoir" and "a gas-liquid separator configured to separate said fluid stream into a gaseous product comprising hydrogen and water vapor, and a liquid comprising water and said metal salt." There is no recitation in the claims of the '657 patent of, among other things, an internal pressure or the spent fuel chamber of the inventions claimed in the present application.

Accordingly, and for at least these reasons, claims 1, 25-29, 31, 32, 46, 47 and 49 are not obvious variations of claims 1-18 of the '657 patent, and withdrawal of this rejection is respectfully requested.

#### The '033 Patent

Claims 25-29, 31, 32, 46, 47, and 49 stand rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-28 of U.S. Patent No. 7,105,033 ("the '033 patent"). Applicants respectfully traverse this rejection.

Claims 1-28 of the '033 patent recite hydrogen gas generation systems comprising "a housing having a hydrogen separation chamber and a fuel storage chamber" separated by a partition, "a catalyst chamber containing a catalyst to promote the reaction of the fuel material," "a fuel conduit for conveying the fuel material from the fuel storage chamber to the catalyst chamber and a outlet conduit to convey the discharged fuel material from the catalyst chamber to the hydrogen separation chamber," "a hydrogen gas outlet in the housing for discharging hydrogen from the hydrogen separation chamber," and "a gas permeable membrane located in at least one of the fuel storage chamber or the hydrogen separation chamber to allow the hydrogen gas to pass through the gas permeable membrane while preventing an aqueous solution to pass through the gas permeable membrane."

Claims 8 to 15 of the '033 patent further recite a "fuel storage chamber enclosing a first flexible bag containing a fuel material capable of generating hydrogen gas and the hydrogen separation chamber enclosing a second flexible bag," while claims 16-18 further recite "a throttle valve located in the fuel conduit" connecting the fuel storage chamber to the catalyst chamber.

Claims 19-24 of the '033 patent recite "a volume exchanging container for use in a hydrogen gas generating system" comprising "a hydrogen separation chamber" having a hydrogen gas outlet and "a fuel storage chamber" having a fuel outlet, and "a gas permeable membrane located in at least one of the fuel storage chamber or the hydrogen separation chamber to allow hydrogen gas to pass through the gas permeable membrane while preventing an aqueous solution to pass through the gas permeable membrane," wherein the hydrogen separation chamber and the fuel storage chamber are separated by a flexible partition.

Claims 25-28 of the '033 patent recite "a fuel container" having a fuel outlet in which a portion of the fuel container comprises "a flexible material adapted to create a pressure on a fuel material contained within the fuel container," "a gas permeable membrane within the fuel container separating the fuel material from a space therein," and "a hydrogen outlet formed in the fuel container."

Amended claims 25-29, 31-32, 46-47 and 49 of the present application are patentably distinct as they recite limitations that are not obvious from the claims of the '033 patent. Claims 25-29, 31-32, 46-47 and 49 of the present application recite an apparatus or arrangement for generating hydrogen comprising, among other things, "a gas conduit between the product container and the fuel container" and "a check valve in communication with said gas conduit."

Accordingly, claims 25-29, 31, 32, 46, 47 and 49 are not obvious variations of claims 1-28 of the '033 patent. For at least these reasons, withdrawal of this rejection is respectfully requested.

Conclusion

The pending claims are believed to be in condition for immediate allowance. If anything further may be required to place these claims in even better form for allowance, the Examiner is cordially invited to telephone the undersigned attorneys for Applicants.

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## Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide

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### Abstract

Sodium borohydride ( $\text{NaBH}_4$ ) reacted slowly with water to liberate 4 mol of hydrogen/mol of the compound at room temperature. Hydrogen generation was accelerated by applying metal–metal oxide catalysts such as Pt– $\text{TiO}_2$ , Pt–CoO and Pt– $\text{LiCoO}_2$ . As the metal crystallites size decreased and the amount increased, the hydrogen generation rate increased. It was indicated that the hydrogen generation rates using Pt and  $\text{LiCoO}_2$  were high compared with those using other metal and metal oxide, respectively. It seemed that a key finding was that use of the supercritical  $\text{CO}_2$  method produced a superior catalyst.

Borohydride ion was stabilized in alkaline solution containing at least 5% by weight of NaOH. Alkaline stabilized solution of  $\text{NaBH}_4$  can be applied as a hydrogen source. We found that Pt– $\text{LiCoO}_2$  worked as an excellent catalyst for releasing hydrogen from the stabilized  $\text{NaBH}_4$  solution. © 2002 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Sodium borohydride; Catalyst; Hydrogen generation; Chemical hydride

### 1. Introduction

In modern society, hydrogen is an important chemical material which is utilized in large amounts in synthetic chemical industries. On the other hand, technologies for utilizing hydrogen as clean energy are considered to assume an important position in order to overcome problems of energy and environment in future. Hence, fuel cells which store hydrogen and operate by using it as fuel have been under development. Such a fuel cell is a battery which is actuated with a gas. Energy obtained upon a reaction of hydrogen and oxygen is directly converted into electric energy. Since such a fuel cell has an efficiency much higher than that of conventional combustion engines, fuel cell vehicle (FCV) is expected as a car having high efficiency [1,2].

Hydrogen can be stored in tanks of compressed [2,3] or liquefied  $\text{H}_2$  [3], or by adsorption on activated carbon [4] and carbon nanotubes [3,5], or in a hydrogen-storing alloy [6]. Among these methods, the hydrogen-storing alloy is considered to play an important role in FCV. For the hydrogen-storing alloy, however, there are also many problems to overcome, such as its heaviness (small amount of storage per unit weight) due to its nature as an alloy, deterioration (the alloy turning into finer particles or changing its structure) upon repeated storage and release, securing of its resources when it includes rare metals.

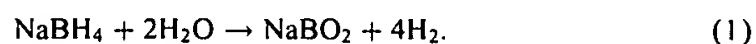
Hence, attention has recently been given to a hydrolysis of chemical hydride which is an alkaline or alkaline earth metal hydride [7]. PowerBall Technologies and Thermo Technologies proposed sodium hydride and lithium hydride, respectively [8–10]. Sodium hydride ( $\text{NaH}$ ) and lithium hydride ( $\text{LiH}$ ) vigorously react with water. Therefore,  $\text{NaH}$  is coated with a resin film, and the film is cut to generate hydrogen in the presence of water on demand [8].  $\text{LiH}$  is prepared as a slurry with light mineral oil and the dispersion has been

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found to be stable for a long periods of time at normal temperature and pressure [9,10].

In view of such circumstances, the hydrolysis of sodium borohydride is of interest in connection with the use of the compound for the generation of hydrogen. Under appropriate conditions, 0.213 g of hydrogen is liberated per 1 g of the compound, as compared with 0.084 g of hydrogen per 1 g of NaH, and 0.254 g of hydrogen per 1 g of LiH, respectively. At ordinary temperatures, only a small amount of the theoretical amount of hydrogen is liberated after the sodium borohydride and water have been mixed [7,11]. The decrease in the initial rate of hydrogen evolution is due to the increasing pH of the solution which in turn is caused by the formation of the basic metaborate ion as shown in Eq. (1) [12,13].



At 25°C the standard-state enthalpy change for the sodium borohydride can be calculated from standard enthalpies  $-188.61 \text{ kJ (NaBH}_4\text{)}$ ,  $-571.66 \text{ kJ (2H}_2\text{O)}$ ,  $-977.0 \text{ kJ (NaBO}_2\text{)}$  and  $0(4\text{H}_2)$  [14]. The standard-state enthalpy change is  $-217 \text{ kJ}$  and such a reaction is exothermic. When sodium borohydride is to be used for generation of hydrogen, rapid reaction is desired. Such a hydrolysis of sodium borohydride has been known to accelerate by catalysts [12,15–17], by acid [12,13], or under elevated temperature [11]. However, addition of acid is undesirable. Conventionally known catalysts are metal halides ( $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ), colloidal platinum, active carbon, Raney nickel [12], Ru supported on ion exchange resin beads [15,16] and fluorinated particles of Mg-based material [17].

Even in the case using such a conventionally known catalyst or under elevated temperature, the hydrogen generation rate and the amount have not been sufficient yet. It is an object of the present paper to provide a catalyst which can achieve a sufficient hydrogen generation rate and amount.

## 2. Experimental

### 2.1. Materials

Sodium borohydride (Rohm and Haas,  $\text{NaBH}_4$ ) was used for the reaction with water. Sodium borohydride is a white crystalline powder, stable in vacuum up to 400°C, and slowly evolves hydrogen at higher temperatures. It slowly absorbs water from moist air to form dihydrate which decomposes slowly to form hydrogen and sodium metaborate. The tetrahedral symmetry of the hydroborate ion in  $\text{NaBH}_4$  has been derived from spectroscopic data. The B–H distance of 0.1255 nm is calculated from the NMR data on crystalline sodium borohydride [13]. The solubility of  $\text{NaBH}_4$  in water at 25°C is 55 g/100 g water [13], but that of  $\text{NaBO}_2$  is 28 g/100 g water. The concentration of  $\text{NaBH}_4$  at 25°C should be below 16 g/100 g water to keep the liquid state of  $\text{NaBO}_2$  which is a byproduct.

Catalysts were prepared by use of the following method using super critical method using carbon dioxide. Fe, Ni, Pd, Ru, Rh or Pt acetylacetonate (Sigma-Aldrich, 10–500 mg) was dissolved into 5 ml of acetone. The resulting solution was introduced into an autoclave, in which 1 g of titania powder (Sachtleben Chemie GmbH, UV100) or cobalt oxide powder ( $\text{CoO}$ , Wako Pure Chemical Industries, Ltd.) and 30 g of dry ice were further added. After being tightly closed, the autoclave was heated and pressurized with  $\text{CO}_2$  at a temperature of 150°C under a pressure of 30 MPa, and held for 2 h to cause the titania powder to carry Fe, Ni, Pd, Ru, Rh or Pt acetylacetonate while in a state where carbon dioxide is a supercritical fluid. Then, the titania powder was held at 105°C for 1 h, to yield a catalyst in which metal is coated on titania (metal content: 0.026–1.3 wt%).

A technique such as a conventional impregnation method was also used to prepare catalysts. Into 33 ml of platinum P salt solution (a nitrate solution of platinum having a platinum content of 50 g/l manufactured by Tanaka Kikinzoku Kogyo K.K.), 100 g of titania powder or lithium cobaltate powder ( $\text{LiCoO}_2$ , Nippon Chemical Industries Co., Ltd., product name Cellseed 5) was introduced to cause the metal oxide powder to carry the nitrate of the noble metal. Then the metal oxide powder was held at 250°C for 5 h. The dried powder was calcinated for 2 h in air at 450°C. Thus a catalyst in which Pt was coated on metal oxide, having Pt content of 1.5 wt%, was obtained.

The following commercial catalysts (metal–metal oxide, metal, metal oxide) were used: platinum–active carbon (Pt: 5 wt%) having a specific surface area of 719  $\text{m}^2/\text{g}$  (Wako Pure Chemical Industries, Ltd.),  $\text{Co}_3\text{O}_4$  (Wako Pure Chemical Industries, Ltd.),  $\text{TiO}_2$  (Sachtleben Chemie GmbH, UV100),  $\text{SiO}_2(\text{UOP})$ ,  $\text{NiO}$  (Wako Pure Chemical Industries, Ltd.),  $\text{LiMn}_2\text{O}_4$  (The Honjo Chemical Corporation),  $\text{TiO}$  (Rare Metallic Co., Ltd.),  $\text{CoO}$  (Wako Pure Chemical Industries, Ltd.),  $\text{Ti}_2\text{O}_3$  (Alfa),  $\text{LiNiO}_2$  (Sumitomo Metal Mining Co., Ltd.),  $\text{LiCoO}_2$  (Nippon Chemical Industries Co., Ltd. Cell seed 5), platinum black (Wako Pure Chemical Industries, Ltd.), platinum–carbon (Pt: 50 wt%, Kishida Chemical Co., Ltd.).

### 2.2. Characterization

The hydrogen generation rate and the amount were determined as follows. Each amount of catalysts [super critical method (Metal– $\text{TiO}_2$ ): 3.8–380 mg, conventional impregnation method (Pt– $\text{TiO}_2$ ): 3.3–33 mg, commercial catalysts: 0.05–10 mg) and 50–200 mg of sodium borohydride were packed into an Erlenmeyer flask having a volume of 100 ml, 0.4–5 g of water were added at room temperature (20–23°C) by use of a syringe, and the hydrogen generation amounts were determined from the change in level of the volumetric burette in a gas analyzer made by Sibata Scientific Technology, Ltd., Japan. The hydrogen generation rate was calculated from the hydrogen gener-

ation amount at the lapse of 3 min after starting the test. The gas generated was identified as hydrogen by a gas chromatograph.

Since  $\text{NaBH}_4$  solution undergoes self-hydrolysis, it was stabilized by maintaining at a high pH. After 50–256 mg of  $\text{Pt-LiCoO}_2$  catalyst was placed in the sealed flask, 30 g of base-stabilized  $\text{NaBH}_4$  solution containing 10%  $\text{NaOH}$ , 20%  $\text{NaBH}_4$  and 70%  $\text{H}_2\text{O}$  was dropped into the catalyst. Then, hydrogen generated was collected and its volume was measured by the water trap method.

The respective average crystallite size of Pt in the catalysts were determined by X-ray diffraction. X-ray diffraction apparatus RAD-B manufactured by Rigaku Corporation was used according to the following process. The catalyst was packed into a sample cell made of glass ( $35 \times 35 \times 2 \text{ mm}^3$ ). The wide angle X-ray diffraction intensity curve was measured with  $\text{CuK}\alpha$  radiation (30 kV, 30 mA) filtered by a graphite monochromator. The crystallite size of Pt [thickness of crystal in a direction perpendicular to the (111) lattice plane]  $L_c$  was determined by the following Scherrer's equation:

$$L_c = K \lambda / \beta \cos \theta, \quad (2)$$

where,  $\beta$  is half-width,  $\lambda$  is wavelength (0.154 nm),  $\theta$  is Bragg angle, and  $K$  is the Scherrer's constant of 0.9.

### 3. Results and discussion

The reaction profile of  $\text{NaBH}_4$  for reaction with water [reaction (1)] carried out at 20–23°C is shown in Fig. 1. Without using catalysts, the amount of hydrogen increases with time and approach to a constant conversion value of 7% because of the increased solution pH. Fig. 1 also shows the hydrogen production profile for the reaction of  $\text{NaBH}_4$  with water using  $\text{Pt-TiO}_2$  catalysts synthesized by different methods. It is revealed that the hydrogen generation rate and the amount are remarkably improved by the catalysts

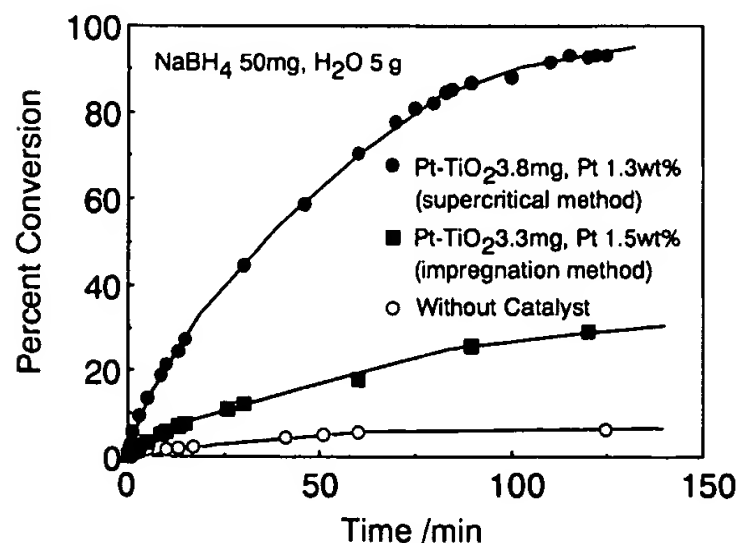


Fig. 1. Hydrogen production profiles for reaction of  $\text{NaBH}_4$  with water using different catalysts at 20–23°C.

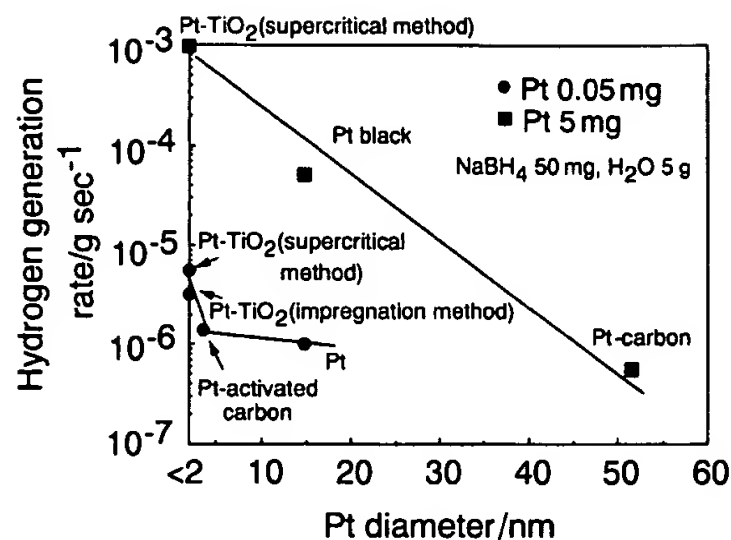


Fig. 2. Influence of Pt size on hydrogen generation rate at 20–23°C.

synthesized particularly using the supercritical method. The catalysts are not consumed during the hydrolysis and are reusable.

After the reaction of  $\text{NaBH}_4$  with water by the catalyst synthesized using the supercritical method, the solution was dried at room temperature over 24 h. X-ray diffraction was used to estimate the structure of the byproduct obtained from the solution. The structure of the product was  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$  by the X-ray diffraction.

The Pt crystallite size was calculated using the Scherrer's equation with the X-ray diffraction data. Fig. 2 shows hydrogen generation rates using various Pt-based catalysts in the Pt content of 0.05–5 mg vs. the Pt crystallite size at 20–23°C. As the crystallite size decreases, the hydrogen generation rate increases and has the maximum value of  $9.7 \times 10^{-4} \text{ g/s}$  at the Pt content of 5 mg below the size of 2 nm. This indicates that the activity of the catalysts increases with the surface area of Pt metal. The diffraction peaks of  $\text{Pt-TiO}_2$  catalysts synthesized using the supercritical method and the impregnation method were not detected, but the hydrogen generation rate of the catalyst synthesized using the supercritical method has highest value, as shown in Fig. 2. It is considered that the Pt crystallite size of the catalyst synthesized using the supercritical method is smaller than that synthesized using the impregnation method. Fig. 2 also shows that increasing the amount of Pt accelerates the hydrogen generation rate for the  $\text{Pt-TiO}_2$  catalyst (supercritical method, Pt: 0.5–5 mg, hydrogen generation rate:  $5.60 \times 10^{-6}$ – $9.65 \times 10^{-4} \text{ g/s}$ ). In the supercritical method,  $\text{Pt-CoO}$  catalyst gave the rate of  $10^{-5} \text{ g/s}$  and higher than that of the  $\text{Pt-TiO}_2$  catalyst (Figs. 1 and 5). We considered that both the metal oxide and the metal might affect the rate of hydrogen generation, so we carried out experiments to study the catalytic activity separately. Fig. 3 shows the hydrogen generation rates for various metals coated on  $\text{TiO}_2$  by the supercritical method. It is shown that Pt has the highest hydrogen generation rate. The hydrogen generation rates for the hydrolysis on different metal oxides are shown

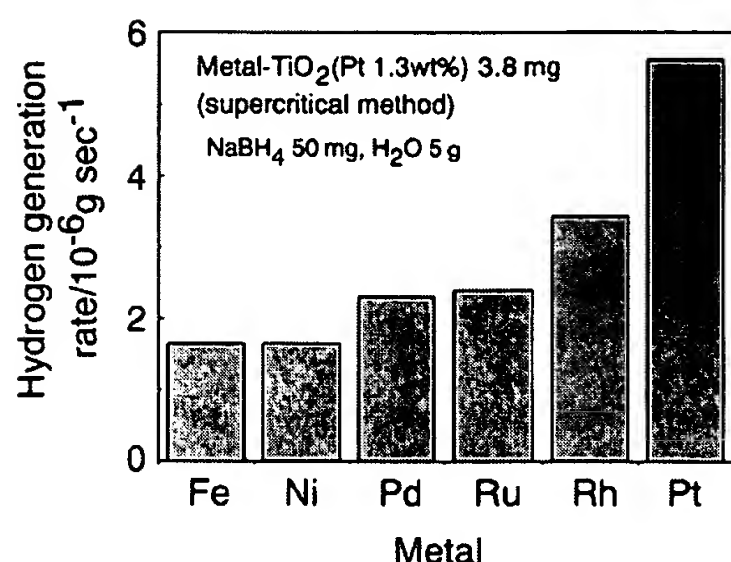


Fig. 3. Hydrogen generation rate using different metals at 20–23 °C.

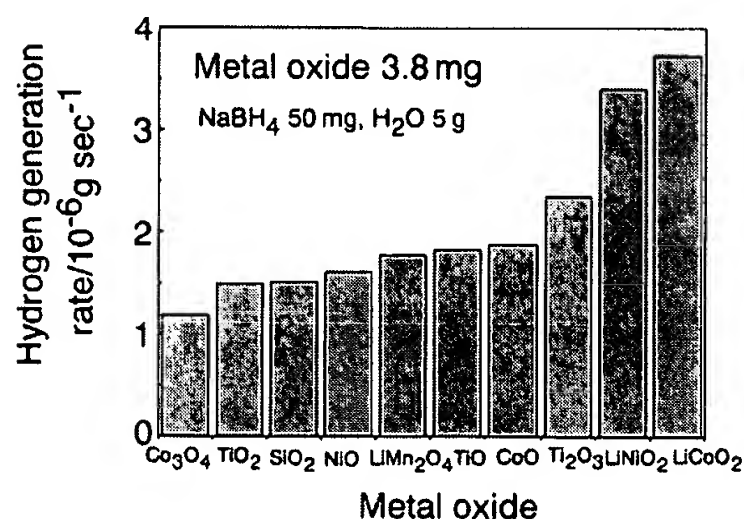
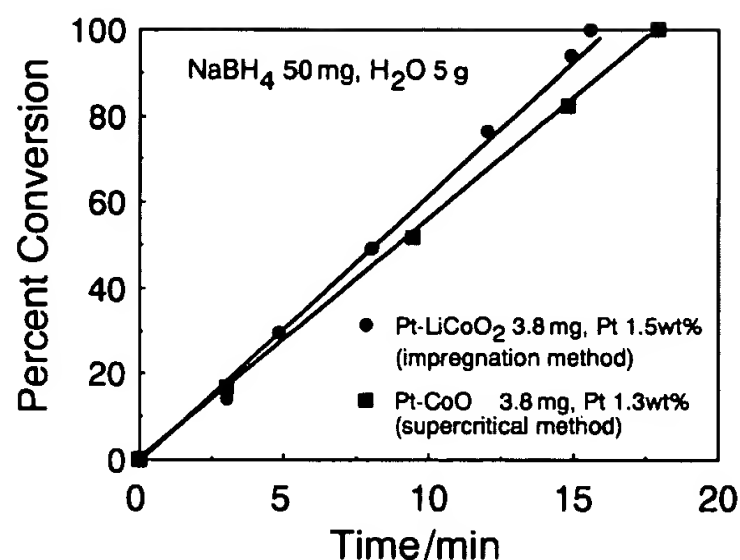
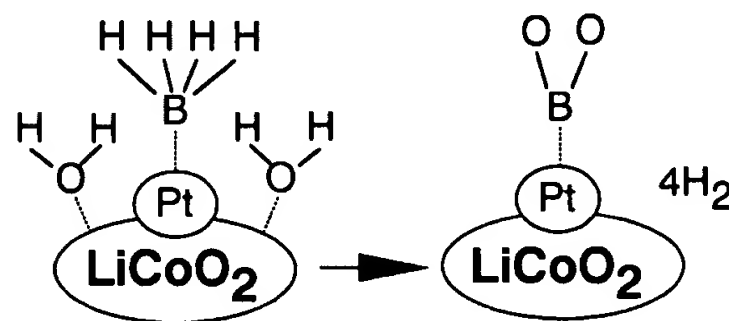


Fig. 4. Hydrogen generation rate using different metal oxides at 20–23 °C.

in Fig. 4. The hydrogen generation rates using LiCoO<sub>2</sub> is higher than that using other carriers.

Using the conventional method, Pt was coated on LiCoO<sub>2</sub>, and Pt–LiCoO<sub>2</sub> catalyst was prepared. Fig. 5 shows the hydrogen production profile for the reaction of NaBH<sub>4</sub> with water using a Pt–LiCoO<sub>2</sub> catalyst. The H<sub>2</sub> generation rate is  $7.9 \times 10^{-6} \text{ g/s}$  and the value is approximately similar to that of Pt–CoO prepared using the supercritical method. The rate using those catalysts is constant and independent of time. We found that 100% of the stoichiometric amount of H<sub>2</sub> was generated by the Pt–LiCoO<sub>2</sub> catalyst synthesized using conventional impregnation method. Furthermore, the hydrogen generation rate is approximately constant and independent of the amount of NaBH<sub>4</sub> (25–100 mg). Thus, the hydrogen generation rate is expressed by the following zero order rate equation:

$$-1/4d[\text{BH}_4^-]/dt = d[\text{H}_2]/dt = k, \quad (3)$$

Fig. 5. Hydrogen production profiles for reaction of NaBH<sub>4</sub> with water using Pt–LiCoO<sub>2</sub> catalyst at 20–23 °C.Fig. 6. Schematic representation of reaction model of NaBH<sub>4</sub> with water on Pt–LiCoO<sub>2</sub> catalyst.

where  $k$  is the rate constant. We have observed zero order kinetics for NaBH<sub>4</sub> hydrolysis reaction. This suggests that the hydrogen generation rate is controlled by the catalyst.

Fig. 6 shows a schematic representation of the reaction model of NaBH<sub>4</sub> with water on the Pt–LiCoO<sub>2</sub> catalyst. Electron is discharged through the catalyst from BH<sub>4</sub><sup>−</sup> ion, and H<sup>−</sup> in BH<sub>4</sub><sup>−</sup> ion is oxidized. On the other hand, this electron reduces the H<sup>+</sup> in water and hydrogen gas is generated (Eq. (4)).



NaBH<sub>4</sub> reacts slowly with water to liberate hydrogen. It has been well known that NaBH<sub>4</sub> is quite stable when maintained at high pH. In our experiment, hydrogen was not generated in 20% NaBH<sub>4</sub>, 10% NaOH, 70% H<sub>2</sub>O solution below the temperature of 35 °C. Hydrogen generation amount using Pt–LiCoO<sub>2</sub> at the base-stabilized NaBH<sub>4</sub> concentration of 20 wt% is shown in Fig. 7, together with that using the Ru catalyst developed by Millennium Cell Co. [15]. The sodium borohydride containing 256 mg of Pt–LiCoO<sub>2</sub> reacts more than 10 times faster than the Ru catalyst reported by Amendola et al. [15]. We found that Pt–LiCoO<sub>2</sub> is an excellent catalyst for hydrogen



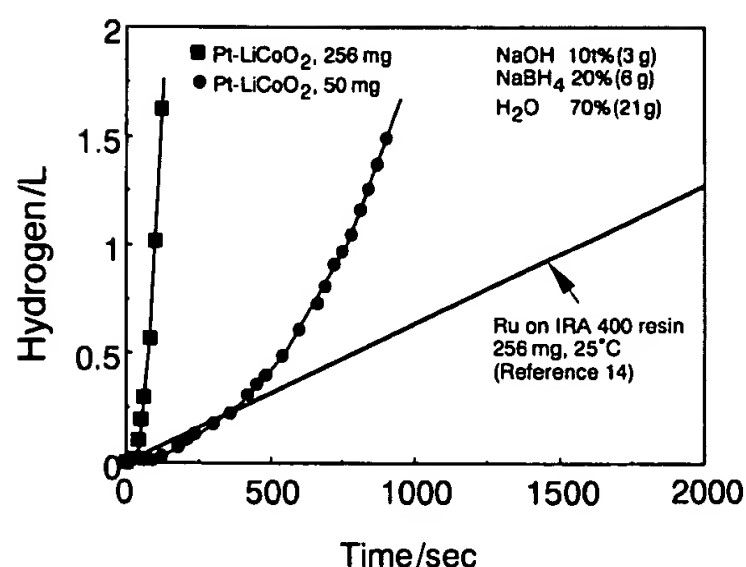


Fig. 7. Volume of H<sub>2</sub> generated as a function of time by different catalysts in 20% NaBH<sub>4</sub>, 10% NaOH, 70% H<sub>2</sub>O solution at 22°C.

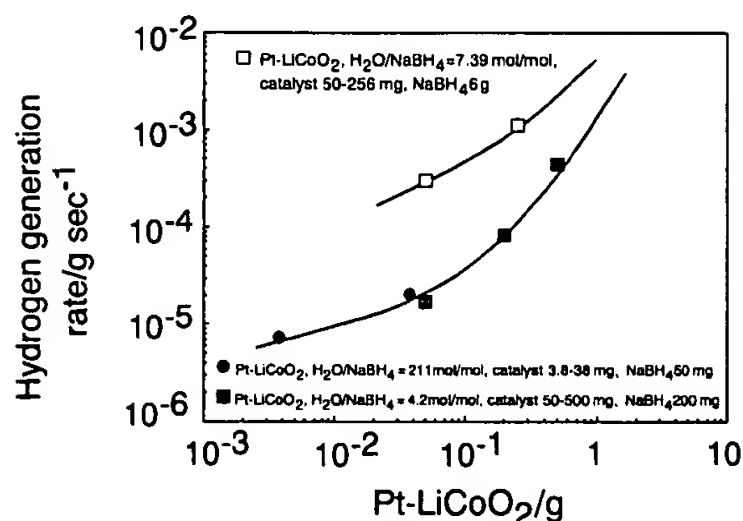


Fig. 8. Influence of Pt-LiCoO<sub>2</sub> amount on hydrogen generation rate at 20–23°C.

generation. The hydrogen generation rate for Pt-LiCoO<sub>2</sub> increases with time, but that for Ru catalysts is constant. It is considered that the reaction temperature increases due to the exothermic reaction in the hydrolysis of NaBH<sub>4</sub>.

The hydrogen generation rate using Pt-LiCoO<sub>2</sub> as a function of the amount of catalyst is plotted in Fig. 8. In the case of high concentration NaBH<sub>4</sub> solution, the rate increases with time elapsed as shown in Fig. 7. We used the maximum value for the hydrogen generation rate in Fig. 8. Pt amount accelerates the hydrogen generation rate. Furthermore, hydrogen generation rate is accelerated when NaBH<sub>4</sub> becomes *g*-scale. This is due to the fact that  $\Delta H$  value with hydrolysis reaction of NaBH<sub>4</sub> is  $-217$  kJ/mol (exothermic reaction).

We can estimate power levels using our catalyst. Assuming a standard PEM fuel cell operates at 0.7 V, generating 1 gH<sub>2</sub>/s is equivalent  $96.5 \text{ kA} \times 0.7 = 68 \text{ kW}$ . Fig. 8 illustrates that our catalyst produces the 0.1–0.34 kW/g Pt-LiCoO<sub>2</sub>

(per 15 mg of Pt) at 20–23°C. Therefore, the amount of the catalyst should be 230–780 g to power a 77.5 kW PEM fuel cell for FCV [2].

In conclusion, the hydrogen generation using sodium borohydride solution was accelerated by applying metal catalyst coated on metal oxide. We found that Pt-LiCoO<sub>2</sub> synthesized using the conventional impregnation method worked as an excellent catalyst for releasing hydrogen from the stabilized NaBH<sub>4</sub> solution.

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